

# Taking retanning to the next level with a new innovative amphoteric polymer

**Christopher S. Tysoe, head of global application and development, Lanxess**

*The amphoteric polymer, Levotan AM, offers the leather industry a new tool for increasing the efficiency of the overall retanning process, saving products, improving fixation and, potentially, fastness, and reducing environmental load. This supports life-cycle extension of existing syntans and polymers. This is without the need for an additional product or extra processing steps. This highly versatile new product is suitable for all types of leather, including especially demanding ones such as automotive, waterproof and white leather, and works both on chrome-tanned and wet white substrates. It has already proven to be an invaluable asset in the tanner's arsenal to help keep leather relevant.*

To avoid any misunderstanding, it is always good to start with a definition. An “amphoteric” polymer has the characteristics of both an acid and a base and is capable of reacting as either. This is not to be confused with lubricating polymers that Lanxess has described as “amphiphilic”, which is having both hydrophilic and hydrophobic (or lipophilic) groups.

Ask any tanner what the most common drawback of traditional retanning polymers is, especially acrylics, and one of the, if not the, most common reply is likely to be “bleaching”. This common tannery term also needs some clarification. Bleaching products work by reacting with dyes (or other organic coloured compounds) and turning them into colourless ones. Most are oxidising agents (they remove electrons from other molecules), others are reducing agents (they donate electrons). Retanning polymers are neither of these. What we commonly refer to as “bleaching” in the tanning industry is more to do with competition for bonding sites between anionic (negatively charged) dyes and similarly charged retanning materials and auxiliaries. As bonding sites are increasingly taken up by retanning agents and auxiliaries, this in turn reduces the number of such sites available for dyes to fix to, hence the correspondingly lighter resulting leather colour or “bleaching”.

Syntans are still indispensable today because rarely is a full polymer retanning requested by tanners or suitable for their customers' end-use articles. Imagine trying to achieve a good buffing, print definition and retention on a rubbery full-polymer retanned chrome leather. Syntans are also necessary to achieve the desired level of dimensional stability (reducing stretch), tightness, fullness and softness, together with improved handle and uniformity. Furthermore, traditional acrylic polymers and large molecular weight resins are commonly known to have limited penetration, and here certain syntans also have a synergistic effect, increasing penetration when required. Vegetable tannins are in general notorious for their high affinity and can lead to a superficial surface build-up. Syntans can be used to control this affinity and prevent over-loading of the grain. However, syntans, too, are usually anionic and thus not only reduce the cationic charge on wet blue but also display

varying degrees of “bleaching”, although with some notable exceptions, such as Tanigan 3LF, which is suited to brilliant white and to jet black leather production.

Normally the type and amount of retanning used is what is necessary to achieve the article so this cannot be simply changed nor reduced to improve build-up and save dyestuff. Simply adding more dye is both costly and wasteful and cationic dyeing auxiliaries add cost, process time, tend to affect certain fastness properties, may not help dye levelness and can increase the risk of bronzing if not applied exactly as prescribed. Until now we are unaware of any product which has been able to solve this conundrum.

## The challenge

There are relatively few references to amphoteric polymers for leather in the literature. The real challenge is to produce a polymer that not only acts like a dye auxiliary but also has retanning functionality. As a dyeing auxiliary it must not only enhance the depth of dyeing but also improve the quality of the dyeing result in terms of levelness and defect coverage. As a retanning agent it must possess a genuine retanning function so that it can replace traditional retanning polymers rather than just add yet another product to the existing recipe.

**Figure 1: amphoteric polymer fixes by high strength coordination or ionic bonds**

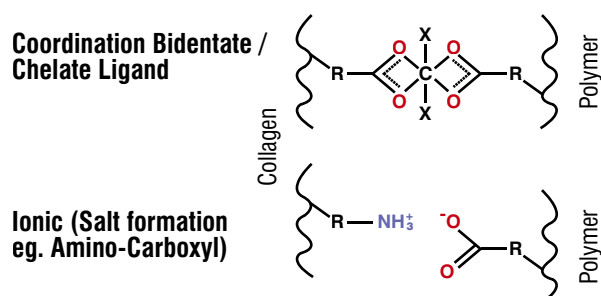
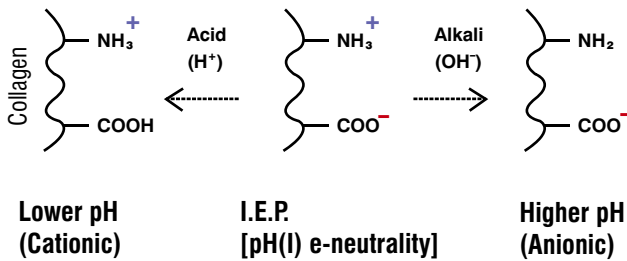
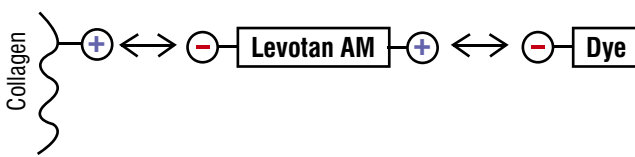


**Figure 2: Effect of pH on Collagen / reactivity of Levotan AM****Figure 3: Levotan AM fixes/retans and provides additional bonding sites for traditional anionic products eg., dyestuffs.**

### Retanning effect and bonding

The amphoteric polymer, Levotan AM, bonds to leather similarly to traditional acrylic and other polymers. It can either fix directly to leather ionically to the amino-groups or, in the case of chrome-tanned leather, in addition via the metal molecule itself (Figure 1). This type of bonding is very strong and can improve certain fastness properties, too, unlike H-bonding of, for example, vegetable tannins or Van der Waals forces of traditional “oil-in-water” fatliquor emulsions, which are weak and easily “broken”.

### How Amphoteric Levotan AM works in application

The IEP [Iso-Electric Point or pH(I)] of collagen is generally given as pH 4.7, whereas chrome-tanned leather has an I.E.P. of between 6.5 and 7.5. This cationic character

is what is particularly good at fixing typical anionic retanning agents and dyes, however the heavier the anionic retanning becomes, this potential will obviously correspondingly decrease.

The IEP of Levotan AM is between pH 4.55 and 4.60 and at this pH the ratio of anionic and cationic groups in the polymer is equal so that electro-neutrality is observed. The product is supplied at a pH of 5.5 – 6.5, which means an excess of anionic charges exist at this pH. Applying the amphoteric polymer in this condition to chrome-tanned leather following “neutralisation” improves the dispersion and penetration of similarly charged retanning products and dyestuffs.

On acidifying for fixation this leads to a pH below the IEPs of both collagen and of the amphoteric polymer, which leads to the optimum formation of cationic charges on both and thus maximum uptake and high exhaustion of anionic retanning products and dyestuffs (Figure 2). The additional bonding sites above and beyond traditional products is illustrated in (Figure 3).

### Application and versatility

In the literature some references can be found to application positions tried for, including now defunct, amphoteric products (Figure 4 - yellow). According to our experience, for example with chrome-tanned leather, we recommend Levotan AM is added before retanning, for approximately 30 minutes. This gives the same degree of penetration and distribution of subsequently added products but better dyeing yield. Alternatively, being a highly versatile product, it can also be added at the end of the dyeing and softening processes in the same float and, following acidification, greatly improves exhaustion of these products too (Figure 4 - both applications in green). Its application in rechroming is not recommended.

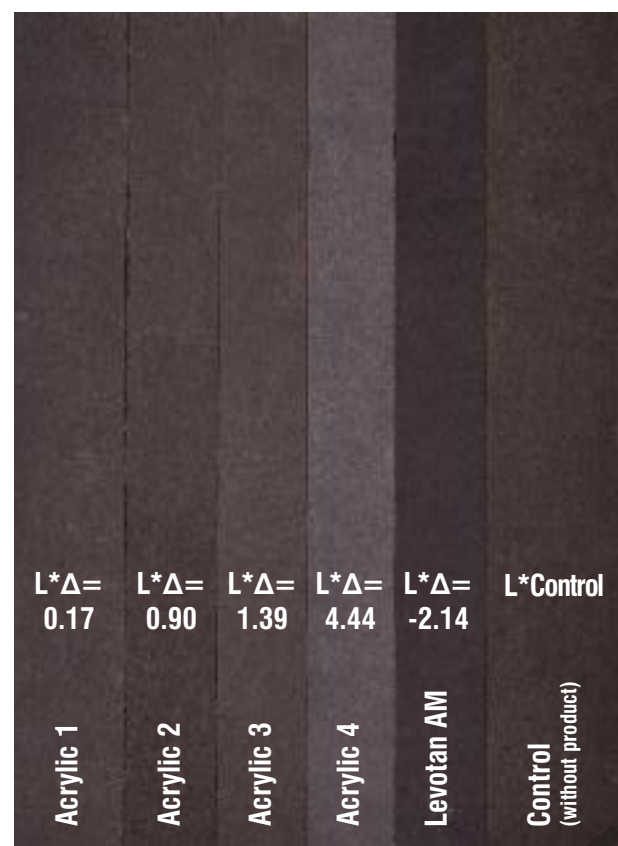
### Benefits

#### Dye build-up and savings

In Figure 5 the amphoteric polymer has been applied 30

**Figure 4: Amphoteric Levotan AM application stages - Past applications (literature: yellow) Levotan AM recommendations (green)**

| Neutralise / Shift I.E.P (Tanigan PAK) |                    |                    |                    |                    |            |            |
|----------------------------------------|--------------------|--------------------|--------------------|--------------------|------------|------------|
| ↓                                      | ↓                  | ↓                  | ↓                  | ↓                  | Levotan AM | ↓          |
| Retanning                              |                    |                    |                    |                    |            |            |
| Amphoteric polymer                     | Amphoteric polymer | Dye I              | Dye I              | Amphoteric polymer | Dye I      | Dye I      |
| ↓                                      | ↓                  | Amphoteric polymer | ↓                  | Dye I              | ↓          | ↓          |
| ↓                                      | Acidify / Fix      |                    |                    |                    | ↓          | ↓          |
| Drain / New float                      |                    |                    |                    |                    | ↓          | ↓          |
| Acidify / Fix                          | ↓                  | Amphoteric polymer | Amphoteric polymer | ↓                  | ↓          | ↓          |
| Dye I                                  | Dye I              | Dye II             | Dye II             | ↓                  | ↓          | ↓          |
| Softening Products                     |                    |                    |                    |                    |            |            |
| ↓                                      | ↓                  | ↓                  | ↓                  | ↓                  | ↓          | Levotan AM |
| Acidify / Fix                          |                    |                    |                    |                    |            |            |
|                                        |                    |                    |                    | Dye II             | Dye II     | Dye II     |

**Figure 5: Levotan AM vs. Standard Acrylic Retanning Polymers**

minutes before retanning. Following dyeing it can clearly be seen that standard acrylics have “bleached” the dyeing to varying degrees versus control. The somewhat surprising fact is that with the amphoteric polymer, in this case, the dye build-up is even higher than the control (resulting in a negative delta, as control is the standard or zero).

Note: to support the illustration in *Figure 5* the CIELAB (International Commission on Illumination 1976) colour space references for L\* only have been used where black (L\*=0) to white (L\*=100). In this case the control sample (without product) has been measured as standard and the deviation, or delta (Δ), from this point has been recorded. All common acrylics have resulted in a lighter dyeing (higher L\* or positive Δ) but in this case the Levotan AM has given a darker-than-control result (lower L\* or negative Δ).

#### Defects reduction

Not only can deeper, more level shades be obtained by applying this amphoteric product, but this can also have a positive effect on the appearance of neck wrinkles and certain grain defects including “light spot”.

#### Ideal for wet white

In the extreme case of mineral-free leather, IEP can reach as low as 4.5-5.5. To achieve the required article, high amounts of retanning agents need to be applied and this leads to less product being adequately fixed in the leather, certain reduced performances and worse exhaustion (worse efficiency). The amphoteric polymer here is invaluable not only because it fixes itself but also increases the exhaustion and fixation of the other products added (*Figure 3*).

#### Ideal for automotive

The exact chemical composition of this fully synthesised polymer is known and so the VOC value has been precisely calculated and is zero. Testing the amphoteric polymer in a standard automotive recipe, comparing it with a common acrylic in parallel-run trials, gave excellent results: Fogging - Reflectometric (%) 93.6 vs. 91.0 (DIN 75210 A) and Gravimetric (mg) 0.43 vs. 0.54 (DIN 75201 B) respectively. For odour - (FLTMBO 131-03 Variant 1-3 23°C/24h, 40°C/24h and 65°C/2h) gave both identical and acceptable results. For heat yellowing (120°C/24h and 100°C/400h) with very good results and for light fastness (ISO105B02 48+72h to 4-5) which is also excellent. Furthermore, this polymer forms a clear, transparent film and has been tested itself for both light (Xenon Test 48hrs) and heat fastness (120°C/24hrs) without any observed change. The “control” common acrylic has been in use for multiple OEMs worldwide for years without odour issues. We can, therefore, conclude that the amphoteric polymer is not able to contribute to any VOC, is acrylic chemistry based being resistant to hydrolysis, increases fixation of other products in retanning and has been independently performance-tested including for smell. This confirms it as suitable for application in automotive leather formulations when such performance criteria are required.

Although the first generation of so-called syntan (“phenolic”) was developed over 100 years ago, it was referred to as an auxiliary and with low fastness properties. We, on the other hand, for decades focused on higher performance solutions and in the 1930s developed the first synthetic, white, light-fast tanning material with the milestone product Tanigan Supra LL and the true vegetable replacement syntans. Where such fastness is demanded in a crust leather, for example, in an automotive application, white or leathersgoods and increasingly today low or “naked” finished leathers, it makes sense to use the latest generation light- and heat-fast syntans, together with the new high-performance amphoteric polymer technology.

#### Ideal for waterproof

Levotan AM has been extensively tested in waterproofing recipes, not only for static water absorption, wicking, Maeser, and water vapour permeability and so on, as expected for this article, but also for a positive effect on tensile and tear-strength and elongation at break. Compared to our top-performing polymers we found no significant contribution to any deterioration in values. Thus, we conclude that this new chemistry can be used in waterproof leather production.

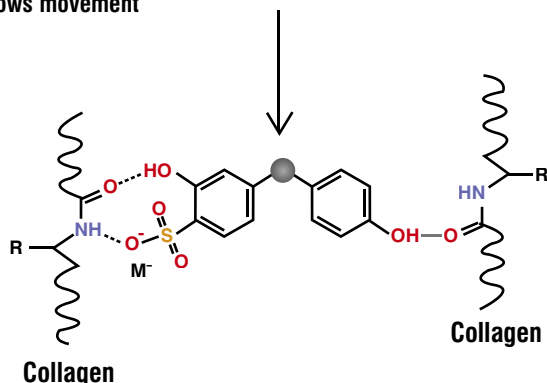
#### Ideal for fashion leather

“Bouncing” or “spongy” nappa is still very much on trend. This leather has a special character, which means when the leather is crushed up, grain inwards in the hand, upon releasing it bounces back to its original flat shape, showing no signs of having been compressed in this way. This demands a super-tight grain that withstands the many hours of milling needed to produce a very soft leather nappa article but with inherent “recoil”.

Although syntans are necessary in this article, they cannot yet be used alone. Syntans fix between amino acid chains resulting in a cross-linking. Syntans typically consist of two “hard spheres” (aromatic rings) linked by a “spring” (typically CH<sub>2</sub>-group) which allows movement, a so-called



**Figure 6: So called “spring” (e.g., CH<sub>2</sub>-group) in syntan which allows movement**



“bouncing effect” at least between the collagen molecules that they separate (*Figure 6*). But this is not enough for “spongy” nappa. (Note: the sulfonate group shown in *Figure 6* can also bind by ionic bonds to collagen amino groups, such as lysine, or to chrome in chrome-tanned leather. In this figure the hydrogen bonds are shown for simplification). Syntans demonstrate vegetable character on “macro” level and thus the leather overall does not spring back.

Polymers, on the other hand, tend to preserve the chrome character of leather, which is elastic-like and so the amphoteric polymer brings the advantages of maintaining

this “bounce” but mitigating the disadvantages of other traditional polymers in the recipe.

#### Cleaner wastewater

This amphoteric polymer improves the exhaustion both of fatliquors and retanning agents reducing the COD and BOD by around 40% (data from a customer's production). This is arguably a more effective way to achieve low values, rather than attempting to look at biodegradability of individual products. It is best to reduce or avoid their discharge in the first place.

Traditional retanning agents, such as vegetable extracts, naturally contain a wide variety of molecules, including those of low tanning-ability (through to non-tannins) which are either difficult or even impossible to exhaust completely in standard retanning, thus putting an increasing load on the wastewater COD. Typically, they are slow to biodegrade and require longer biological treatment times giving a higher COD to BOD ratio. Here the amphoteric polymer increases the uptake and potentially reduces the amount of retanning products needed.

#### Lighter-weight leather

With greater efficiency in the use of retanning products, especially those which normally add weight such as certain traditional fatliquors, this lightweight polymer is expected to contribute to the achievement of lower-density leathers and work is ongoing to highlight this point. ☺

## Relax, You're Protected!

### Chemtan® M-55 Fire Retardant



# CHEMTAN

Tel: (603) 772-3741

www.CHEMTAN.com • info@CHEMTAN.com